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## The Molecular Structure of Nitrogen Dioxide. A Reinvestigation by Electron Diffraction\*

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An investigation of the structure of the nitrogen dioxide molecule has been made by the electron diffraction method. The interpretation of the photographs, which showed rings extending to values of  $q$  of nearly  $100(q=40/\lambda \sin\theta/2)$ , leads to the following structural parameter values:  $N-O=1.20\pm0.024$ ,  $\angle O-N-O=132\pm3^\circ$ . These values are discussed briefly and compared with those obtained by other methods.

#### INTRODUCTION

IN recent years the molecular structure of nitrogen dioxide has been the subject of numerous investigations but, aside from general agreement on a non-linear symmetrical structure with a wide bond angle and a multiplicity corresponding to only the odd electron, the conclusions have been surprisingly divergent. This is true of the dielectric constant measurements on the  $NO_2-N_2O_4$  system, which have lead variously to the conclusions that both nitrogen dioxide and nitrogen tetroxide have small constant dipole moments of the order of  $0.4\times10^{-18}$  e.s.u., that of nitrogen tetroxide being the greater,<sup>1,2</sup> and that nitrogen dioxide has a moment of this magnitude which decreases with increasing temperature while nitrogen tetroxide has a zero moment.<sup>3</sup> It is especially true of the bond angle and bond distance estimates and determinations, which naturally concern us directly. However, Giauque and Kemp's<sup>4</sup> comprehensive considerations of the

equilibrium measurements<sup>5</sup> on the dissociation of nitrogen dioxide in connection with spectroscopic data for nitric oxide,<sup>6</sup> oxygen,<sup>7</sup> and nitrogen dioxide rule out the suggestion of Zeise<sup>8</sup> that the molecule has a multiplicity of 4. This suggestion is likewise ruled out by the results of the magnetic susceptibility measurements of Havens,<sup>9</sup> as was pointed out by Harris and King.<sup>10</sup>

From consideration of an assumed electronic structure Pauling<sup>11</sup> predicted 1.18A for the nitrogen-oxygen distance and  $140^\circ$  for the angle  $O-N-O$ . On the assumption of a valence potential function and a frequency assignment suggested by the infrared spectrum Penney and Sutherland<sup>12</sup> obtained the value  $114^\circ$  for the bond angle. With a similar assumption but a slightly

\* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1156.

<sup>1</sup> C. T. Zahn, *Physik. Zeits.* **34**, 461 (1933).

<sup>2</sup> R. W. Schultz, *Zeits. f. Physik* **109**, 517 (1938).

<sup>3</sup> J. W. Williams, G. H. Schwinger, and C. H. Winning, *J. Am. Chem. Soc.* **58**, 197 (1936).

<sup>4</sup> W. F. Giauque and J. D. Kemp, *J. Chem. Phys.* **6**, 40 (1938).

<sup>5</sup> Especially those of M. Bodenstein and Lindner, *Zeits. f. physik. Chemie* **100**, 82 (1922).

<sup>6</sup> H. L. Johnston and A. T. Chapman, *J. Am. Chem. Soc.* **55**, 153 (1933).

<sup>7</sup> H. L. Johnston and M. K. Walker, *J. Am. Chem. Soc.*, **55**, 172 (1933).

<sup>8</sup> H. W. Zeise, *Zeits. f. Elektrochemie* **42**, 785 (1936).

<sup>9</sup> G. G. Havens, *Phys. Rev.* **41**, 337 (1932).

<sup>10</sup> L. Harris and G. W. King, *J. Chem. Phys.* **8**, 775 (1940).

<sup>11</sup> L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 270.

<sup>12</sup> W. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc. A* **156**, 654 (1936).

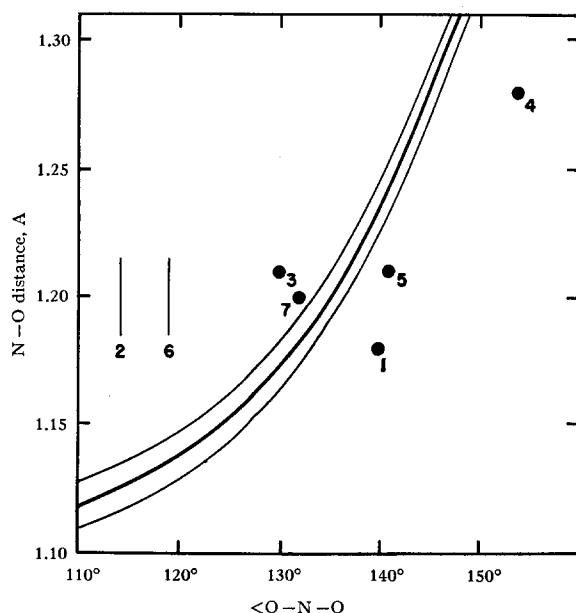


FIG. 1. Results of various estimates and determinations of the structure of nitrogen dioxide. 1: Pauling; 2: Penney and Sutherland; 3: Maxwell and Mosley; 4: Harris and King; 5: Spurr; 6: Herzberg; 7: This work. The curves show values consistent with the revised product of the moments of inertia and its limit of error.

different assignment of frequencies Herzberg<sup>13</sup> obtained the value  $119^\circ$  for the bond angle. An early electron-diffraction study by Maxwell, Mosley, and Deming<sup>14</sup> was unable to give reliable structural information, but a subsequent investigation of Maxwell and Mosley<sup>15</sup> gave the values 1.21A and  $130^\circ$  for the two structural parameters; however a subsequent treatment of the data of Maxwell and Mosley by Spurr<sup>16</sup> gave the same value for the bond distance but the much higher value of  $141^\circ$  for the bond angle. On the other hand, after a partial analysis of the ultraviolet spectrum, Harris and King<sup>10</sup> reported 1.28A for the bond distance and  $154^\circ$  for the bond angle.

The calculations of Giauque and Kemp,<sup>4</sup> which were based on spectroscopic data<sup>6,7</sup> and equilibrium measurements of the dissociation of nitrogen dioxide,<sup>5</sup> gave a reliable value for the

<sup>13</sup> G. W. Herzberg, *Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, New York, 1945), p. 170.

<sup>14</sup> L. R. Maxwell, V. Mosley, and L. Deming, *J. Chem. Phys.* **2**, 331 (1934).

<sup>15</sup> L. R. Maxwell and V. Mosley, *J. Chem. Phys.* **8**, 738 (1940).

<sup>16</sup> R. Spurr, quoted in Yost and Russell, *Systematic Inorganic Chemistry* (Prentice-Hall, New York, New York, 1944), p. 27.

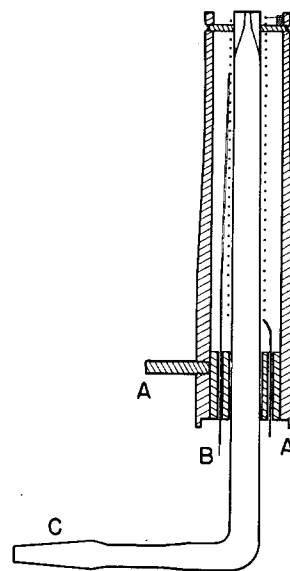


FIG. 2. High temperature nozzle used in this investigation. A: leads to heating coil; B: leads to thermocouple; C: standard taper joint to fit the tube containing the sample.

product of the moments of inertia, from which may be obtained an equation giving corresponding values of the bond distance and bond angle. Since the accepted values for natural constants have changed significantly since Giauque and Kemp made their calculations, we have calculated the change in the value of the product of the moments of inertia which results when the revised constants<sup>13</sup> are used.<sup>17</sup> We find that the value of  $I_1 I_2 I_3$  must be revised upwards by 4.3 percent to  $1.50 \times 10^{-116} \text{ g}^3 \text{ cm}^6$  if the vibrational assignment for nitrogen dioxide used by Penney and Sutherland<sup>12</sup>—the one used by Giauque and Kemp—is used; if the vibrational assignment of Herzberg<sup>13</sup> is used the value of  $I_1 I_2 I_3$  must be revised upwards 3.0 percent. (An upward revision of  $I_1 I_2 I_3$  of 2.6 percent is required by the changes in the rotational and translational parts of the calculation alone.) The value of  $I_1 I_2 I_3$

<sup>17</sup> In calculating the changes in the values of the thermodynamic quantities  $(F^\circ - H_0^\circ)/T$  of nitric oxide and oxygen it was assumed that whatever change in these values would result from changing the constants is identical with the change in the calculated result for a rigid rotator harmonic oscillator approximation, plus a  $120 \text{ cm}^{-1}$  doubling of all levels of nitric oxide, since the original calculations (see references 7 and 8) made use of the spectroscopically observed levels and a recalculation on that basis would be somewhat complicated.

$=1.50 \times 10^{-116} \text{ g}^3 \text{ cm}^6$  is probably known to about 5 percent.

We have reinvestigated the structure of nitrogen dioxide by the electron diffraction method; we find  $1.20 \pm 0.02 \text{ \AA}$  for the nitrogen-oxygen distance and  $132 \pm 3^\circ$  for the bond angle. This result together with the various results mentioned above are shown in Fig. 1.

### EXPERIMENTAL

Nitrogen dioxide was prepared by heating lead nitrate in a stream of oxygen. The gas was condensed with dry ice and then twice distilled in an atmosphere of oxygen in an all-glass apparatus.

Electron diffraction photographs were taken with the apparatus described by Brockway.<sup>18</sup> An all-glass high-temperature nozzle of special design shown in Fig. 2, was used to heat the gas sample before the photographs were taken. The length of the chimney, which was heated to  $140^\circ$  before each exposure, was sufficient to insure that the dissociation of nitrogen tetroxide to

nitrogen dioxide was complete before the gas entered the diffraction chamber.

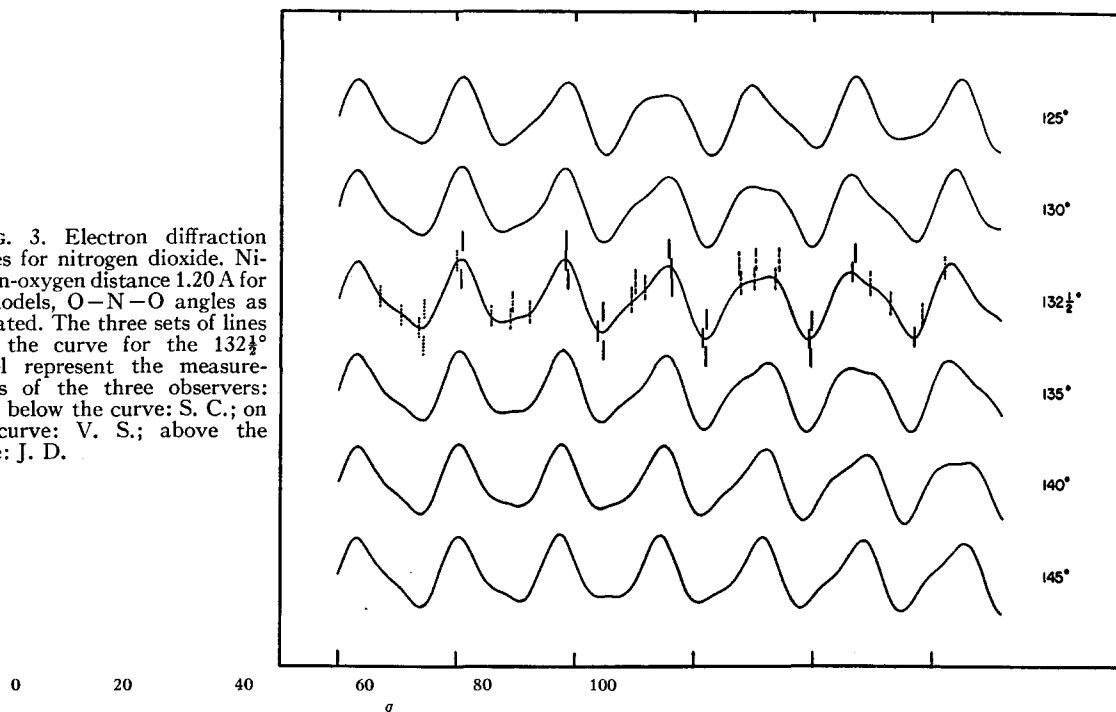
The photographs were examined on a viewing box equipped with a lamp of adjustable intensity, and, for the outer rings, two or more good photographs were superimposed. Measurements of the diffraction features were made in the usual way.

Because of the simplicity of the problem the customary radial distribution treatment was omitted and only the correlation method<sup>19</sup> was used in interpreting the photographs. The formula

$$I(q) = \sum_{ij} \frac{Z_i Z_j}{r_{ij}} \sin\left(\frac{\pi}{10} r_{ij} q\right)$$

was used to calculate simplified theoretical intensity curves, shown in Fig. 3, for six models with  $\text{N}-\text{O}=1.20 \text{ \AA}$  and  $\angle \text{O}-\text{N}-\text{O}=125^\circ, 130^\circ, 132\frac{1}{2}^\circ, 135^\circ, 140^\circ$ , and  $145^\circ$  respectively. These calculations were made on International Business Machines with punched cards.<sup>20</sup>

FIG. 3. Electron diffraction curves for nitrogen dioxide. Nitrogen-oxygen distance  $1.20 \text{ \AA}$  for all models,  $\text{O}-\text{N}-\text{O}$  angles as indicated. The three sets of lines with the curve for the  $132\frac{1}{2}^\circ$  model represent the measurements of the three observers: those below the curve: S. C.; on the curve: V. S.; above the curve: J. D.



<sup>18</sup> L. O. Brockway, *Rev. Mod. Phys.* 6, 234 (1936). Wave length calibration: C. S. Lu and E. W. Malmberg, *Rev. Sci. Instr.* 14, 2181 (1937). The lattice constants of zinc oxide given by them in  $kX$  units were converted to angstrom units.

<sup>19</sup> L. Pauling and L. O. Brockway, *J. Chem. Phys.* 2, 867 (1934).

<sup>20</sup> P. A. Schaffer, Jr., V. Schomaker, and L. Pauling, *J. Chem. Phys.* 14, 659 (1946).

TABLE I. Results of measurements of electron diffraction photographs of nitrogen dioxide.

Observer	Average value of $q_{132^\circ}/q_{\text{obs.}}$	Average deviation	Number of features included in average
S. C.	0.996	0.006	6
J. D.	0.999	0.004	7
	0.999	0.008	12
V. S.	1.003	0.007	7
	1.002	0.008	16

## RESULTS

As may be seen in Fig. 3, the character of the features of the theoretical intensity curves changes rapidly with change in bond angle. Comparison of these curves with the appearance of the photographs fixes the bond angle at  $132 \pm 3^\circ$ . The features at  $q \cong 55$ , 70, and 85 were particularly useful in fixing the bond angle. The relative heights of the components which comprise these three doublet maxima are in best agreement with the appearance of the photographs at  $132^\circ$ . At larger bond angles the outer components of the rings at  $q \cong 70$  and 85 are too strong; at smaller bond angles the inner components of the rings at  $q \cong 55$  and 70 are too strong, and the outer component of the ring at  $q \cong 85$  disappears.

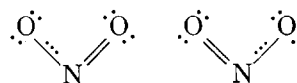
Between seven and twenty-five measurements were made on each of the features measured by the three observers. The average values of  $q_{132^\circ}$  (obtained by interpolation) divided by  $q_{\text{obs.}}$  are presented in Table I. We consider those obtained from the measurements indicated by the solid lines in Fig. 3 to be the most reliable. The averages obtained from these measurements together with those indicated by the dashed lines in Fig. 3 include features which are more difficult to measure; it is interesting that the average values of  $q_{132^\circ}/q_{\text{obs.}}$  are not changed appreciably by including these measurements. The averages  $q/q_{\text{obs.}}$  and the average deviations were calculated for the measurements of the smaller sets of features of each of the three observers for the  $125^\circ$ ,  $130^\circ$ ,  $135^\circ$ , and  $140^\circ$  models also. In each case there is

a convincing minimum in the average deviations very near  $132^\circ$ , substantiating the value of the bond angle determined by the correlation treatment. Measurements on the extreme inner and outer features, indicated by dotted lines in Fig. 3, were considered by the respective observers to be unreliable, and were not included in any averages. The averaged results of the three observers give for the nitrogen-oxygen distance 1.20A. In consideration of the average deviations shown in Table I and the uncertainty in the bond distance arising from the uncertainty in the bond angle obtained by the correlation treatment, we estimate the limit of error of the nitrogen-oxygen distance to be  $\pm 0.02\text{A}$ .

## DISCUSSION

Our results are in fairly good agreement with the previous electron diffraction results of Maxwell and Mosley;<sup>15</sup> we feel that ours are somewhat more accurate because we observed features at larger  $q$  values than did the previous investigators. Moreover, our results are in better agreement with the product of the moments of inertia. It is apparent that the structures derived from the spectroscopic considerations<sup>10, 12, 13</sup> are considerably in error.

The structure found for the nitrogen dioxide molecule is in good qualitative agreement with the discussion of Pauling,<sup>11</sup> who predicted a bond distance slightly larger than that of a nitrogen-oxygen double bond, and a bond angle intermediate between  $125^\circ 16'$ , the double bond value, and  $180^\circ$ , corresponding to the following resonating structure for the molecule:



## ACKNOWLEDGMENT

We wish to thank Mr. Kenneth Hedberg for his assistance in preparing the photographs.